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(54) COMPOSITE MATERIAL FOR BRAZING AND BRAZING STRUCTURE



(57)Abstract:

PROBLEM TO BE SOLVED: To provide a material for brazing in which the corrosion resistance and the oxidization resistance of a brazing filler metal part with which joined members are brazed are improved and to provide a brazing structure which is suitable for the flow passage structure of a heat exchanger.

SOLUTION: The structure is provided with a base plate 11 which is formed by a stainless steel member 11, a Fe-atom-diffusion-suppressing layer 12 which is formed by a Ni-Cr alloy which consists essentially of Ni and includes 10 to 30 mass % Cr, and further provided with, when necessary, a brazing filler metal layer 13 which is formed by a Cu-based brazing filler metal formed as a lamination on the Fe-atom-diffusion-suppressing layer 12. The diffusion of Fe atoms in the base plate into the brazing filler metal which is melted during a brazing process is suppressed by the Fe-atom-diffusion-suppressing layer, and a proper amounts of Ni and Cr are diffused into the brazing filler metal part, thus the excellent corrosion resistance and the oxidization resistance are given to the brazing filler metal part.

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CLAIMS

[Claim(s)]

[Claim 1] Laminating formation is carried out on the front face of the substrate formed with corrosion-resistant steel materials, and said substrate. It is the composite for brazing and soldering equipped with Fe atom diffusion control layer which controls that Fe atom is spread in a wax material side from said substrate in case the brazing and soldering of the joint material are carried out by Cu system wax material formed with Cu radical alloy which uses pure Cu or Cu as a principal component. Said Fe atom diffusion control layer is the composite for brazing and soldering which used nickel as the principal component and was formed with the nickel-Cr alloy containing Cr:10 - 30mass%.

[Claim 2] Composite for brazing and soldering with which the laminating of the wax material layer formed of said wax material on said Fe atom diffusion control layer was carried out and which was indicated to claim 1.

[Claim 3] Said Cu system wax material is the composite for brazing and soldering which used Cu as the principal component and was formed with the aluminum addition Cu radical alloy containing aluminum:1 - 5mass% and which was indicated to claims 1 or 2.

[Claim 4] The thickness of said Fe atom diffusion control layer is 5 micrometers. Composite for brazing and soldering which it is above and which was indicated in any 1 term of claims 1-3.

[Claim 5] It has the substrate formed with the 1st joint material which has the substrate formed with corrosion-resistant steel materials, and

corrosion-resistant steel materials. It has the touched 2nd joint material which will shine through the wax material section to said 1st joint material. Said 1st joint material It has Fe atom diffusion control layer which controls that Fe atom is spread in the wax material section from the substrate of said 1st joint material in case the brazing and soldering of said 2nd joint material are carried out. This Fe atom diffusion control layer uses nickel as a principal component, and it is formed with the nickel-Cr alloy containing Cr:10 - 30mass%. Said wax material section is the brazing-and-soldering structure which used Cu as the principal component and was formed with the Cu-nickel-Cr alloy which contains Cr:10 - 15mass% nickel:15 - 25mass%.

[Claim 6] It has the substrate formed with the 1st joint material which has the substrate formed with corrosion-resistant steel materials, and corrosion-resistant steel materials. It has the touched 2nd joint material which will shine through the wax material section to said 1st joint material. Said 1st joint material It has Fe atom diffusion control layer which controls that Fe atom is spread in the wax material section from the substrate of said 1st joint material in case the brazing and soldering of said 2nd joint material are carried out. This Fe atom diffusion control layer uses nickel as a principal component, and it is formed with the nickel-Cr alloy containing Cr:10 - 30mass%. Said wax material section is the brazing-and-soldering structure which used Cu as the principal component and was formed with the Cu-nickel-Cr-aluminum alloy which contains aluminum:1 - 5mass% Cr:8 - 15mass% nickel:15 - 25mass%.

[Claim 7] Brazing-and-soldering structure by which the passage divided by these joint material was formed between said 1st joint material and said 2nd joint material and which was indicated to claims 5 or 6.

[Claim 8] Said 2nd joint material is the brazing-and-soldering structure in which it has Fe atom diffusion control layer which controls that Fe atom is spread in the wax material section from the substrate of said 2nd joint material in case the brazing and soldering of said 1st joint material and 2nd joint material are carried out, and this Fe atom diffusion control layer was formed with said nickel-Cr alloy and which was indicated in any 1 term of claims 5-7.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the composite for brazing and soldering used as brazing-and-soldering structure suitable as passage structure of heat exchangers, such as a radiator and a gas cooler, and its material.

[0002]

[Description of the Prior Art] The interest about an environmental problem is increasing internationally in recent years, and purification of the exhaust gas of an automobile is strongly required increasingly as part of that. Various kinds of purges, such as a thermal reactor which is made to already afterburn exhaust gas and sets CO and HC to CO₂ and H₂O as a cure against exhaust gas purification of an automobile, and a catalytic converter, are put in practical use. Conventionally, in an exhaust gas purge etc., the brazing and soldering of the joint material which consists of stainless steel material which has corrosion resistance are carried out by Cu system wax material, and the heat exchanger used in a hot corrosive gas ambient atmosphere is manufactured. The corrosion resistance good copper wax in which said Cu system wax material has the melting point of 1000 degrees C or more, Mn:5-20% indicated by JP, 60-72695, A, or the wax material which becomes a remainder real target from Cu has been used further nickel:1-5%.

[0003] Recently, the corrosive environment in a heat exchanger is becoming severe much more by change of an exhaust gas presentation etc., and the problem of the corrosion by the condensate of exhaust gas is also produced. For this reason, much more corrosion resistance improvement is called for from the brazing-and-soldering section to which the joint material which constitute the passage structure of a heat exchanger is joined by wax material. To such a demand, as indicated by the international public presentation WO 00/No. 45987 Fe atom diffusion control layer formed in the substrate with which this

invention persons consist of stainless steel material with nickel radical alloy which uses pure nickel or nickel as a principal component, And constituting the passage structure of a heat exchanger is proposed using joint material made from the composite for brazing and soldering and this which carried out the laminating of the wax material layer formed with Cu radical alloy which uses pure Cu or Cu as a principal component. According to this composite for brazing and soldering, by Fe atom diffusion control layer, it is controlled that Fe atom is spread in the wax material section from stainless steel material in the case of brazing and soldering, and nickel of optimum dose can be spread in the wax material section from Fe atom diffusion control layer, a Cu-nickel alloy can be formed, and the corrosion resistance of the wax material section can be raised.

[0004]

[Problem(s) to be Solved by the Invention] As mentioned above, the corrosion resistance in the wax material section of a heat exchanger was able to be raised by using the composite for brazing and soldering equipped with Fe atom diffusion control layer. However, it is inadequate as endurance just to raise the corrosion resistance of the wax material section in the heat exchanger which performs heat exchange of elevated-temperature exhaust gas, and the further subsequent research showed that there was a bad influence for the whole processing system incorporating a heat exchanger. That is, when fluids which should be carried out heat exchange, such as exhaust gas, were high-temperature-corrosion nature fluids and the oxidation resistance of the wax material section ran short, the oxide film exfoliated from the front face of the wax material section, and it flowed to the downstream of a heat exchanger, and degradation of bonding strength not only arises by the oxidation loss of the wax material section, but it went to it, various kinds of processors formed in the downstream were soiled, and the problem of degrading the engine performance became clear.

[0005] This invention was made in view of this problem, and aims at offering the brazing-and-soldering structure excellent in the corrosion resistance and the oxidation resistance in the charge of brazing-and-soldering material which can give corrosion resistance and oxidation resistance excellent in the wax material section, and the wax material section in brazing-and-soldering structures, such as passage structure of a heat exchanger.

[0006]

[Means for Solving the Problem] The substrate in which the composite for brazing and soldering by this invention was formed with corrosion-

resistant steel materials, It has Fe atom diffusion control layer which controls that Fe atom is spread in a wax material side from said substrate in case the brazing and soldering of the joint material are carried out by Cu system wax material formed in the front face of said substrate with Cu radical alloy which laminating formation is carried out and uses pure Cu or Cu as a principal component. Said Fe atom diffusion control layer uses nickel as a principal component, and is formed with the nickel-Cr alloy containing Cr:10 - 30mass%. Hereafter, the unit of a component is only displayed by %.

[0007] According to this composite, since laminating formation of the Fe atom diffusion control layer is carried out at the substrate, it is prevented by the wax material section in the brazing-and-soldering structure which will shine using this composite and which touched by Fe atom diffusion control layer that Fe atom is spread in the wax material section from a substrate in the case of brazing and soldering, and it can prevent corrosion resistance degradation of the wax material section in it. Furthermore, since Fe atom diffusion control layer is formed with the specified quantity **** nickel-Cr alloy in Cr, 15 - 25% of nickel and the Cu-nickel-Cr alloy containing 10 - 15% of Cr can be formed in the wax material section by making the wax material section diffuse nickel and Cr from Fe atom diffusion control layer in the case of brazing and soldering. nickel of said Cu-nickel-Cr alloy raises the corrosion resistance of the wax material section further, and said Cr forms Cr system oxide film in the front face of the wax material section, and raises oxidation resistance. For this reason, the wax material section of brazing-and-soldering structure should be excelled in corrosion resistance and oxidation resistance.

[0008] As a desirable mode of said composite for brazing and soldering, laminating formation of the wax material layer formed of said Cu system wax material on said Fe atom diffusion control layer can be carried out. In case the brazing and soldering of the joint material are carried out by preparing a wax material layer in one, it is not necessary to prepare wax material separately, and brazing work nature can be raised.

[0009] Moreover, as a desirable mode of said composite for brazing and soldering, Cu can be used as a principal component for Cu system wax material, and it can form with Cu radical alloy containing aluminum:1-7%. By using this aluminum content Cu radical alloy, aluminum system oxide film is formed in Cr system oxide-film bottom, and oxidation resistance can be remarkably raised with the oxide film of a duplex.

[0010] Fe atom diffusion control layer in said composite for brazing and soldering is 5 micrometers. Considering as the above thickness is

desirable. 5 micrometers By considering as the above thickness, it can fully control that Fe atom of a substrate carries out solid phase diffusion of the Fe atom diffusion control layer, and invades into the wax material section in the case of brazing and soldering, and corrosion resistance degradation by diffusion invasion of Fe atom of the wax material section can fully be prevented.

[0011] The 1st joint material which has the substrate in which the brazing-and-soldering structure by this invention was formed with corrosion-resistant steel materials, Have the substrate formed with corrosion-resistant steel materials, and it has the touched 2nd joint material which will shine through the wax material section to said 1st joint material. It has Fe atom diffusion control layer which controls that Fe atom diffuses said 1st joint material in the wax material section from the substrate of said 1st joint material in case the brazing and soldering of said 2nd joint material are carried out. This Fe atom diffusion control layer uses nickel as a principal component, and it is formed with the nickel-Cr alloy containing Cr:10 - 30mass%, and said wax material section uses Cu as a principal component, and is formed with the Cu-nickel-Cr alloy containing nickel:15-25% and Cr:10-15%.

[0012] According to this brazing-and-soldering structure, since Fe atom diffusion control layer formed with the nickel-Cr alloy which contains Cr in a substrate as an indispensable component is formed, the 1st joint material The alloying by nickel of the specified quantity which Fe atom could control carrying out diffusion invasion in the wax material section from the substrate of the 1st joint material, and was further formed of diffusion of nickel from Fe atom diffusion control layer, and Cr when carrying out the brazing and soldering of the 2nd joint material, Corrosion resistance and oxidation resistance excellent in the wax material section are given by formation of Cr system oxide film by Cr of the specified quantity. By this, brazing-and-soldering structure becomes the thing equipped with the outstanding endurance.

[0013] In said brazing-and-soldering structure, it is desirable to form with the Cu-nickel-Cr-aluminum alloy which the wax material section uses Cu as a principal component, and contains nickel:15-25%, Cr:8-15%, and aluminum:1-5%. By making the wax material section contain aluminum of the specified quantity, compound formation of the aluminum oxide film can be carried out at Cr system oxide-film bottom, and oxidation resistance can be raised more. What is necessary is to contain aluminum 1 to 5% and just to use the aluminum addition Cu radical alloy which uses Cu as a principal component as Cu system wax material used for

brazing and soldering, in order to include aluminum of the specified quantity in the wax material section.

[0014] In said brazing-and-soldering structure, the passage divided by these joint material between said 1st joint material and said 2nd joint material can be formed. By forming this passage, the fluid by which heat exchange is carried out to this passage, or the medium which carries out heat exchange can be poured, and the passage structure of the heat exchanger equipped with the outstanding endurance can be offered.

Moreover, the bad influence by exfoliation of an oxide film can be prevented to the equipment attached to the downstream of said passage.

[0015] Moreover, in said brazing-and-soldering structure, like [said part II material] said 1st joint material, in case the brazing and soldering of said 1st joint material and 2nd joint material are carried out, Fe atom diffusion control layer which controls that Fe atom is spread in the wax material section from the substrate of said 2nd joint material can be prepared, and this Fe atom diffusion control layer can be formed with said nickel-Cr alloy. By this, it can prevent that Fe atom carries out diffusion invasion in the wax material section from the 2nd joint material, and the solderability of the 2nd joint material can be improved.

[0016]

[Embodiment of the Invention] Drawing 1 shows the composite 1 for brazing and soldering concerning the operation gestalt of this invention, laminating formation of the Fe atom diffusion control layer 12 is carried out at one side of the plate-like substrate 11, and laminating formation of the wax material layer 13 is carried out on it. Since laminating formation of the wax material layer 13 is carried out on Fe atom diffusion control layer 12, in case this composite 1 for brazing and soldering performs brazing work, the complicated activity of attaching the wax material prepared separately between the joint material which is the objects of brazing and soldering becomes unnecessary, and it is excellent in brazing work nature.

[0017] Said substrate 11 is formed by stainless steel material, such as ferritic-stainless-steel material of the corrosion resistance good iron steel materials 304, for example, SUS of JIS, the austenitic-stainless-steel material of SUS316 grade, SUS430, and SUS434 grade.

[0018] said Fe atom diffusion control layer 12 -- Cr: -- it is preferably formed Cr:15-25% 10 to 30% with the nickel-Cr alloy which uses Remainder nickel as an essential component. This nickel-Cr alloy does not generate the sludge which that melting point is higher than the melting point of Cu system wax material which forms the wax material

layer 13, and dissolves excluding Fe with Cu nickel and whose Cr are the principal components of said wax material, therefore is easy to become the origin of corrosion. Although said nickel-Cr alloy consists of the remainder nickel besides Cr and the unescapable impurity element which are an important component in this invention typically, it dissolves to nickel and workability as a nickel-Cr alloy is not spoiled, but if it is the element which does not degrade the property of the wax material section after brazing and soldering, the minute amount addition is permitted.

[0019] By diffusing the wax material section produced by melting of the wax material layer 13 on the occasion of brazing and soldering about 15 to 25%, and making it dissolve, nickel of said nickel-Cr alloy raises the corrosion resistance of the wax material section. On the other hand, Cr raises oxidation resistance, in order to form Cr system oxide film in the front face by diffusing said wax material section 10 to 15%, and making it dissolve. Cr content of said nickel-Cr alloy is difficult for diffusion of Cr of said optimum dose in the wax material section at less than 10% in the case of brazing and soldering, and the oxidation resistance of the wax material section comes to fall. On the other hand, if it exceeds 30%, workability will deteriorate and the diffusion to the wax material section will become excessive. Consequently, the amount of Cr(s) in the wax material section becomes easy to produce the segregation of Cr in super-15%, and corrosion resistance comes to fall on the contrary. For this reason, Cr content of the nickel-Cr alloy which forms Fe atom diffusion control layer 12 is more preferably made into 15 - 25% 10 to 25% 10 to 30%.

[0020] The thickness of said Fe atom diffusion control layer 12 is 5 micrometers. It is 8 micrometers preferably above. It is 10 micrometers more preferably above. It is good to consider as the above. Although it considers as about 1100-1250 degrees C so that brazing-and-soldering temperature may be mentioned later, when carrying out brazing and soldering using said composite for brazing and soldering, it is 5 micrometers also by the brazing and soldering in this elevated temperature. If there is thickness of extent, the diffusion depressor effect of Fe atom of considerable extent can be acquired, and it is 10 micrometers. If it is, the diffusion to the wax material section of Fe atom can be prevented nearly completely.

[0021] It is formed of Cu system wax material which consists of a Cu radical alloy which uses pure Cu or Cu as a principal component as said wax material layer 13. As said Cu radical alloy, a constituent makes a dissolution condition completely, for example, can use a Cu-nickel alloy

and a Cu-Mn-nickel alloy. There should just be about 85% or more of Cu contents in general. The presentation which uses less than [nickel:15%] and Remainder Cu as an essential component with said Cu-nickel alloy is desirable. nickel -- 15% -- super- -- ** -- the melting point of ** which will be taken becomes high and brazing work becomes difficult. It dissolves to Cu, and if it is the element which does not spoil the workability of wax material, and the property of the wax material section after brazing and soldering, the minute amount addition is permitted by said Cu radical alloy.

[0022] Said Cu system wax material has the desirable aluminum addition Cu radical alloy with which aluminum was added 2 to 4% especially preferably 1 to 5%. By adding aluminum, since aluminum system oxide film comes to be further formed in Cr system oxide-film bottom (wax material side) formed in the front face of the wax material section formed of brazing and soldering and the oxide film of a duplex is formed, oxidation resistance improves remarkably. If formation of aluminum system oxide film is difficult for the amount of aluminum at less than 1% and it exceeds 5% on the other hand, processing of an aluminum addition Cu radical alloy becomes difficult, and it can be used no longer as wax material. Since oxidation resistance improves sharply according to an operation of aluminum when using an aluminum addition Cu radical alloy as wax material, oxidation resistance sufficient by making Cr content in the wax material section into 8 - 15% can be acquired. In addition, said Cr system oxide film and aluminum system oxide film can be checked by EPMA.

[0023] Although the clad method by the pressure welding is generally applied to laminating formation of Fe atom diffusion control layer 12 to said substrate 11, various approaches, such as plating, thermal spraying, and PVD, CVD, are also applicable. Without generating the pinhole which poses a problem in plating, if the clad of a substrate 11 and the Fe atom diffusion control layer 12 is carried out with a pressure welding, both can be unified easily and it excels in industrial productivity. Moreover, the thickness of Fe atom diffusion control layer 12 is also easily controllable only by adjusting the rolling reduction in the case of a pressure welding. The wax material layer 13 is usually joined by the pressure welding on Fe atom diffusion control layer 12 by which the laminating was carried out to the substrate 11. What is necessary is to make each material of a substrate 11, Fe atom diffusion control layer 12, and the wax material layer 13 pile up mutually respectively, to carry out a pressure welding, and just to carry out homogenizing if needed, when carrying out the clad of the three layers with a pressure welding.

[0024] Although what is necessary is just to make brazing-and-soldering temperature in the case of using said brazing-and-soldering composite into the temperature of under the melting point of the metal which forms Fe atom diffusion control layer above the melting point of Cu system wax material, it is usually preferably made into about 1150-1200 degrees C about 1100-1250 degrees C. At less than 1100 degrees C, being spread in the wax material section, in case nickel and Cr are brazing and soldering takes time amount from Fe atom diffusion control layer, and it is inferior to productivity. on the other hand -- the temperature of 1250-degree-C ** -- unnecessary -- quantity -- the expensive furnace at which it was too tepid and the damage on a heating furnace was very [violently or] rich in thermal resistance is needed, and it is not suitable for industrial production anyway. If the holding time in brazing-and-soldering temperature is about 1100-1250 degrees C, it is good at about 10 - 50 minutes. When the composite for brazing and soldering is processed into a proper configuration in the case of the temperature maintenance at the time of this brazing and soldering, annealing of that substrate 11 is also performed to coincidence.

[0025] As mentioned above, although the operation gestalt explained the composite for brazing and soldering of this invention, this invention is not restrictively interpreted by this. For example, with the above-mentioned operation gestalt, although laminating formation of Fe atom diffusion control layer 12 and the wax material layer 13 was carried out at one side of a substrate 11, when using it for an application by which the brazing and soldering of the joint material are carried out to both sides of a substrate, the laminating of Fe atom diffusion control layers 12 and 12 and the wax material layers 13 and 13 can be carried out to both sides of a substrate 11 like composite 1A for brazing and soldering shown in drawing 2. Moreover, when preparing wax material separately, it is not necessary to carry out the laminating of the wax material layer 13.

[0026] Here, the corrosion resistance of the wax material section of the brazing-and-soldering structure which will shine using the above-mentioned composite 1 for brazing and soldering and which touched, and oxidation-resistant results of an investigation are explained. The composite 1 for brazing and soldering used for investigation uses the SUS304 stainless steel plate (0.4mm of board thickness) of JIS as a substrate 11, and carries out laminating formation of the wax material layer 13 which consists of Fe atom diffusion control layer 12 which consists of a nickel-Cr alloy on it and pure Cu, or a Cu Al alloy with a pressure welding. The amount of nickel in the Cu-nickel-Cr alloy of the

amount of Cr(s) in the nickel-Cr alloy of Fe atom diffusion control layer 12 of the composite used about each sample, the amount of aluminum in the Cu Al alloy of the wax material layer 13, brazing-and-soldering conditions (temperature, holding time), and the wax material section or a Cu-nickel-Cr-aluminum alloy, the amount of Cr(s), and the amount of aluminum are shown in Table 1 (the unit of the amount of elements is mass%). In addition, although it tried to form a wax material layer with a Cu-7%aluminum alloy, since this alloy had bad workability and it was not able to process tabular, it did not come to manufacture the composite for brazing and soldering.

[0027] This composite was bent to L typeface so that the wax material layer 13 side might become outside, and the L form member was manufactured. As shown in drawing 3, the longitudinal side of the L form member 5 was piled up, the brazing and soldering of the pair of this L form member were carried out, and the brazing-and-soldering structure sample of T typeface was obtained. Thus, while measuring the average presentation of the wax material section by EPMA using each manufactured sample, a corrosion resistance test and the anti-oxidation sex test were performed.

[0028] a corrosion resistance test prepares the simulation water of condensation of the following presentation which simulated the exhaust-gas condensate, and carries out the visual observation of the T form top face of a sample where the wax material section after 500hr immersion exposed each sample in the 100-degree C simulation water of condensation, and good (B) and its surface corrosion field are [what / has corrosion / be nothing / thing / 20% or less of] improper for A (A) and a surface corrosion field in 20% super-**- it estimated as (C).

- Simulation water-of-condensation presentation (pH4.4)

Cl-: 20ppm, SO42-:350ppm, NO3-:150ppm, NH4+:700ppm, formic-acid:500ppm, an acetic acid: 700 ppm [0029] On the other hand, the mass change after carrying out 50hr maintenance of each sample at 650 degrees C in atmospheric air is measured, it ** in the area on the top face of T form of the sample which the wax material section exposed, and the anti-oxidation sex test is 2 lcm. The amount of oxidation increase and decrease of a hit was calculated. In the wax material section of the sample after a trial, when a scaling coat fell out in powder, the powder oxide film was removed and measured with the brush. In this case, the amount of oxidation increase and decrease is shown by the negative value. When the stabilization oxide film is formed in the front face of the wax material section, the amount of oxidation increase and decrease is shown by the positive value. the amount of oxidation increase and decrease is

a positive value, and oxidation-resistant evaluation is excellent in the case not more than SUS304 (about two 1 mg/cm) of a substrate, an EQC, or it — (AA) — Although A (A) and an oxide film had not resulted in omission the case where there was a little more augend than SUS304, the case where omission of a failure (C) and an oxide film were remarkable was estimated for the case where a part of good (B) and oxide film are omitted in the case where the increment in mass is large as the failure (CC). These results are collectively shown in Table 1.

[0030]

[Table 1]

試料 No.	Fe原子 拡散抑制層 Cr%	ろう材層 Al%	ろう接条件			ろう材組成			耐食性 評価	耐酸化性	
			温度 ℃	時間 min		NI%	Cr%	Al%		増減量 mg/cm ²	評価
* 1	—	—	1180	20		20	—	—	A	-18.5	CC
* 2	2	—	1180	20		19	1	—	A	-18.4	CC
* 3	5	—	1180	20		18	2	—	A	-10.2	CC
* 4	10	—	1180	20		18	8	—	A	-8.8	C
5	15	—	1180	20		18	10	—	A	3.2	B
6	20	—	1180	20		17	12	—	A	2.8	A
7	25	—	1180	20		14	14	—	B	2.0	A
* 8	10	—	1100	20		8	5	—	C	-9.48	CC
* 9	10	—	1200	20		18	8	—	A	-8.70	C
10	10	—	1250	20		22	10	—	A	3.1	B
11	20	—	1100	40		15	11	—	A	3.0	B
* 12	20	—	1250	40		28	18	—	C	1.13	A
21	10	1	1180	20		18	8	1	A	4.3	B
22	10	2	1180	20		18	8	2	A	2.7	A
23	10	3	1180	20		17	8	3	A	0.56	AA
24	10	5	1180	20		16	8	4	A	0.41	AA
25	20	1	1180	20		17	12	1	A	1.12	A
26	20	2	1180	20		17	12	2	A	0.42	AA
27	20	3	1180	20		17	12	3	A	0.30	AA
28	20	5	1180	20		16	12	4	A	0.26	AA

(注) 試料No. に「*」を付したものは比較例、他は発明例

[0031] Sample No. of Table 1 When the brazing and soldering of the brazing-and-soldering temperature are carried out from 1-7 at 1180 degrees C which is fully generous from the heating critical temperature, In the example of invention (sample No.5-7) which formed Fe atom diffusion control layer with the nickel-Cr alloy contained Cr:15 to 25%, it turns out that the amount of 20-minute room [about] Cr(s) [in /

comparatively / by short-time maintenance / the wax material section] becomes 10 - 14%, and it has good corrosion resistance and good oxidation resistance. On the other hand, from sample No.8-10, when Fe atom diffusion control layer is comparatively made into 10% of the amount of low Cr(s), comparatively, by short-time heating, it can secure 10% as an amount of Cr(s) of the wax material section, and by raising brazing-and-soldering temperature to 1250 degrees C near the heating critical temperature shows that oxidation resistance is also acquired for the thing of practical use level. But No.11 show that form Fe atom diffusion control layer for brazing-and-soldering temperature with a nickel-Cr alloy with the high amount of Cr(s) also as 1100 degrees C, and good oxidation resistance is acquired by lengthening brazing-and-soldering time amount comparatively. Moreover, from sample No.21-28, when the amount of aluminum used the aluminum-Cu alloy wax material which is 2 - 5% especially 1 to 5% as wax material, it was checked that oxidation resistance improves by leaps and bounds.

[0032] Next, the passage structure of a heat exchanger is explained as an operation gestalt of the brazing-and-soldering structure using the composites 1 and 1A for brazing and soldering concerning the above-mentioned operation gestalt as a material.

[0033] Drawing 4 is the perspective view showing the passage structure of the heat exchanger concerning the 1st operation gestalt. In 2 sets of plate members which the plate member 21-1 of the lot countered and arranged and 21-2 separate predetermined spacing, are arranged at two or more set parallel, and adjoin mutually In the example of drawing, the fin member 22 of the shape of bellows by which crookedness formation of the cross section was carried out at the wave is interposed between the plate member 21-2 of the top group bottom, and the plate member 21-1 of the bottom group top which countered this plate member 21-2, and has been arranged. In addition, said plate member corresponds to the 1st joint material of the structure for brazing and soldering of this invention, and a fin member corresponds to the 2nd joint material.

[0034] Let the plate member 21-1 of said lot, and the space section between 21-2 be the medium passage where heat exchange media, such as cooling water, flow. On the other hand, let the subspace section of a large number divided by said fin member 22 be the gas passageway to which the high-temperature-corrosion nature gas by which heat exchange is carried out, such as exhaust gas, flows between the plate member 22-2 of the top group bottom, and the plate member 21-1 of a bottom group top.

[0035] As for each fin member 22, the brazing and soldering of the bottom of a wave crevice and the top face of the plate member 21-1 of

the bottom which pinches the fin member 22 where the topmost part of wave heights and the inferior surface of tongue of the plate member 21-2 of the bottom which pinches this fin member 22 will shine through the wax material section are similarly carried out through the wax material section by being touched. In the following explanation, the plate member 21-1 of a lot and 21-2 may be explained, using 21 as a sign of a plate member, when not distinguishing both.

[0036] The material in front of the brazing and soldering of said plate member 21 is processed into magnitude with the proper composite 1 for brazing and soldering which has the structure shown in drawing 1, and the quality of the material. Said fin member 22 is processed into a wave in the sheet metal which consists of the same stainless steel as the substrate 11 of the composite 1 for brazing and soldering. Suppose that the same sign as the composite 1 for brazing and soldering is attached [section / that / each / laminating] about the material for plate members for convenience, using the same sign as said plate member 21 of explanation.

[0037] In order to manufacture a heat exchanger using the material 21 for plate members, and the fin member 22 So that the fin member 22 may contact the wax material layer 13 of the material 21 for plate members Pile up by turns, and assemble the fin member 22 and the material 21 for plate members like drawing 4, and they carry out shape retention. This assembly under with the melting point of Fe atom diffusion control layer 12 in a vacuum or a reducing gas ambient atmosphere at the temperature more than the melting point of the wax material layer 13, usual, and 1100-1250 degrees C Grade heating maintenance is carried out for 10 - 50 minutes so that the essential component of the wax material section may serve as Remainder Cu nickel:15-25% and Cr:10-15% (it is 8 - 15% when carrying out brazing and soldering by the aluminum addition Cu radical alloy wax material mentioned later). The wax material layer 13 of the material 21 for plate members fuses, and the brazing and soldering of the fin member 22 are carried out to Fe atom diffusion control layer 12 by which the pressure welding was carried out to the substrate 11 by this through the wax material section equipped with the good corrosion resistance containing said nickel and the amount of Cr(s), and oxidation resistance. Oxidation resistance can be raised remarkably, without aluminum of tales doses containing mostly in the wax material section, and degrading corrosion resistance by using the aluminum content Cu radical alloy of aluminum 1 to 5% as Cu system wax material. In this case, if there is at least 8% of the amounts of Cr(s), they can acquire good oxidation resistance.

[0038] Drawing 5 is the sectional view showing the passage structure of the heat exchanger concerning the 2nd operation gestalt. This passage structure is having honeycomb structure, and two or more laminatings of the concave heights material 31 by which the crevice 32 and heights 33 of trapezoidal shape continued by turns, and fabrication was carried out to the wave are carried out in the vertical direction, and it is constituted. ** which attaches the sign of 31-1 and 31-2 to the concave heights material of a certain pair by which contiguity arrangement of the explanation was carried out for convenience up and down. In addition, said concave heights material 31-1 and 31-2 correspond to the 1st joint material of the brazing-and-soldering structure of this invention, and the 2nd joint material.

[0039] As for the concave heights material 31-1 and 31-2 comrades which adjoin up and down, the brazing and soldering of the external surface (inferior surface of tongue) of the crevice 32 of the upper wave member 31-1 and the external surface (top face) of the heights 33 of the lower concave heights material 31-2 are carried out mutually. Between the heights 33 of the upper concave heights material 31-1, and the crevice 32 of the lower concave heights material 31-2, much space sections of 6 square-shape cross section are formed of this. This space section is made into the medium passage W where gas-passageway G to which high-temperature-corrosion nature gas, such as exhaust gas, flows, and heat exchange media, such as cooling water, flow, and gas-passageway G and the medium passage W are arranged by turns in the example of drawing at right and left.

[0040] Fabrication of the composite 1A for brazing and soldering which has the cross-section structure which shows the material of the concave heights material 31 of said heat exchanger in drawing 2, and the quality of the material is carried out to proper magnitude concave convex. Suppose that the same sign as composite 1A for brazing and soldering is attached [section / that / each / laminating] about the material for concave heights material for convenience, using the same sign as said concave heights material 31 of explanation.

[0041] What is necessary is to carry out a laminating, as the inferior lamella section 32 of the upper material 31-1 for concave heights material and the superior lamella section 33 of the lower material 31-2 for concave heights material are piled up and it is shown in drawing 5, and just to carry out heating maintenance in a vacuum or a reducing gas ambient atmosphere like the 1st operation gestalt, in order to manufacture a heat exchanger using said material 31 for concave heights material. The material 31-1 for concave heights material by which

opposite arrangement was carried out up and down, the wax material layer 13 of 31-2, and 13 comrades fuse and unify, and brazing and soldering are mutually carried out to the specified quantity nickel and Cr pan through the wax material section containing aluminum by this.

[0042] The brazing-and-soldering structure of this invention is not restrictively interpreted according to the passage structure of the heat exchanger of this 1st and 2nd operation gestalt. For example, the laminating number of stages of the plate member 21 of the 1st operation gestalt and the laminating number of stages of the concave heights material 31 of the 2nd operation gestalt can be freely set up according to a demand. Moreover, with the above-mentioned 1st operation gestalt, although the fin member 22 used stainless steel sheet metal, it may use what carried out laminating formation of the Fe atom diffusion control layer by using stainless steel sheet metal as a substrate also about the fin member, and the thing in which the wax material layer was formed on Fe atom diffusion control layer, still like drawing 1. By forming Fe atom diffusion control layer also about a fin member, it can prevent carrying out diffusion invasion to the wax material which Fe atom fused from the substrate of a fin member on the occasion of brazing and soldering, and corrosion-resistant degradation of the brazing-and-soldering section to which the brazing and soldering of the fin member were carried out can be prevented.

[0043] Moreover, although the clad of the wax material layer 13 besides Fe atom diffusion control layer 12 is carried out to the composites 1 and 1A for brazing and soldering used as a material, the wax material layer 13 is not necessarily required of the passage structure of the heat exchanger of the above-mentioned 1st and 2nd operation gestalt. In this case, Cu system wax material prepared separately is attached between the material for plate members, and a fin member, or between the materials for concave heights material, and should just carry out brazing and soldering.

[0044]

[Effect of the Invention] Since it has Fe atom diffusion control layer formed with the nickel-Cr alloy which the composite for brazing and soldering of this invention used nickel as the principal component at the substrate formed with corrosion-resistant steel materials, and contained Cr 10 to 30% In case the brazing and soldering of the joint material are carried out by Cu system wax material, while being able to control diffusion of Fe atom which degrades corrosion resistance in the wax material section, nickel and Cr of optimum dose can be diffused easily, and the corrosion resistance of the wax material section and

oxidation resistance can be raised. For this reason, that endurance can be raised by constituting the passage structure of the heat exchanger used for the bottom of high-temperature-corrosion ambient atmospheres, such as exhaust gas, using the composite for brazing and soldering of this invention.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the fragmentary sectional view of the composite for brazing and soldering concerning the operation gestalt of this invention.

[Drawing 2] It is the fragmentary sectional view of the composite for brazing and soldering concerning other operation gestalten.

[Drawing 3] It is the sectional view of the brazing-and-soldering structure of a T character configuration used for corrosion resistance and the anti-oxidation sex test.

[Drawing 4] It is the fragmentary sectional view showing the passage structure of the heat exchanger concerning the 1st operation gestalt of the brazing-and-soldering structure of this invention.

[Drawing 5] It is the fragmentary sectional view showing the passage structure for heat exchangers concerning the 2nd operation gestalt of the brazing-and-soldering structure of this invention.

[Description of Notations]

- 1 1A Composite for brazing and soldering
- 11 Substrate
- 12 Fe Atom Diffusion Control Layer
- 13 Wax Material Layer
- 21-1, 21-2 Plate member

22 Fin Member
31 Concave Heights Material

[Translation done.]

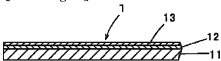
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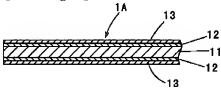
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DRAWINGS

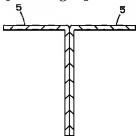
[Drawing 1]



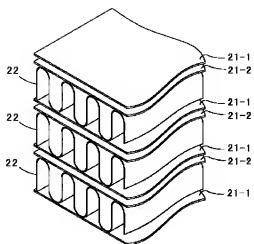
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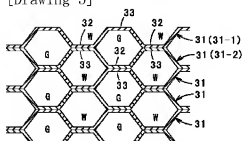
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]

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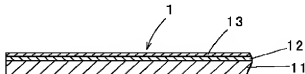
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(54) 【発明の名称】 ろう接用複合材及びろう接構造

(57) 【要約】

【課題】 接合部材がろう接されるろう材部の耐食性、耐酸化性を向上させることができるろう接用材料、および熱交換器の流路構造として好適なろう接構造を提供する。

【解決手段】 ステンレス鋼材により形成された基板11と、Niを主成分とし、Crを10～30mass%含有するNi-Cr合金により形成されたFe原子拡散抑制層12と、さらに必要によりFe原子拡散抑制層12の上に積層形成されたCu系ろう材によって形成されたろう材層13を備える。前記Fe原子拡散抑制層により、ろう接の際に基板中のFe原子が溶融したろう材部に拡散することが抑制され、また適量のNi、Crをろう材部に拡散させることができ、ろう材部に優れた耐食性、耐酸化性を付与することができる。



【特許請求の範囲】

【請求項 1】 耐食性鋼材により形成された基板と、前記基板の表面に積層形成され、純 Cu あるいは Cu を主成分とする Cu 基合金で形成された Cu 系ろう材によって接合部材をろう接する際に前記基板から F e 原子がろう材側に拡散するのを抑制する F e 原子拡散抑制層とを備えらるろう接用複合材であって、

前記 F e 原子拡散抑制層は N i を主成分とし、C r : 10 ~ 30 mass% を含有する N i - C r 合金で形成された、ろう接用複合材。

【請求項 2】 前記 F e 原子拡散抑制層の上に前記ろう材によって形成されたろう材層が積層された、請求項 1 に記載したろう接用複合材。

【請求項 3】 前記 Cu 系ろう材は Cu を主成分とし、A l : 1 ~ 5 mass% を含有する A l 添加 Cu 基合金で形成された、請求項 1 または 2 に記載したろう接用複合材。

【請求項 4】 前記 F e 原子拡散抑制層の厚さが 5 μ m 以上である、請求項 1 から 3 のいずれか 1 項に記載したろう接用複合材。

【請求項 5】 耐食性鋼材で形成された基板を有する第 1 接合部材と、耐食性鋼材で形成された基板を有し、前記第 1 接合部材にろう材部を介してろう接された第 2 接合部材とを備え、

前記第 1 接合部材は、前記第 2 接合部材がろう接される際に前記第 1 接合部材の基板から F e 原子がろう材部に拡散するのを抑制する F e 原子拡散抑制層を有し、この F e 原子拡散抑制層は N i を主成分とし、C r : 10 ~ 30 mass% を含有する N i - C r 合金で形成され、前記ろう材部は Cu を主成分とし、N i : 15 ~ 25 mass %、C r : 10 ~ 15 mass% を含有する Cu - N i - C r 合金で形成された、ろう接構造。

【請求項 6】 耐食性鋼材で形成された基板を有する第 1 接合部材と、耐食性鋼材で形成された基板を有し、前記第 1 接合部材にろう材部を介してろう接された第 2 接合部材とを備え、

前記第 1 接合部材は、前記第 2 接合部材がろう接される際に前記第 1 接合部材の基板から F e 原子がろう材部に拡散するのを抑制する F e 原子拡散抑制層を有し、この F e 原子拡散抑制層は N i を主成分とし、C r : 10 ~ 30 mass% を含有する N i - C r 合金で形成され、前記ろう材部は Cu を主成分とし、N i : 15 ~ 25 mass %、C r : 8 ~ 15 mass%、A l : 1 ~ 5 mass% を含有する Cu - N i - C r - A l 合金で形成された、ろう接構造。

【請求項 7】 前記第 1 接合部材と前記第 2 接合部材との間にこれらの接合部材によって画された流路が形成された、請求項 5 または 6 に記載したろう接構造。

【請求項 8】 前記第 2 接合部材は前記第 1 接合部材と第 2 接合部材とがろう接される際に前記第 2 接合部材の

基板から F e 原子がろう材部に拡散するのを抑制する F e 原子拡散抑制層を有し、この F e 原子拡散抑制層が前記 N i - C r 合金によって形成された、請求項 5 から 7 のいずれか 1 項に記載したろう接構造。

【発明の詳細な説明】

【0001】

【発明が属する技術分野】本発明は、ラジエーター、カスクローラーなどの熱交換器の流路構造として好適なろう接構造およびその素材として使用されるろう接用複合材に関する。

【0002】

【従来の技術】近年、国際的に環境問題への関心が高まっており、その一環として自動車の排気ガスの浄化が強く要求されるようになってきている。自動車の排気ガス浄化対策として、すでに排気ガスを再燃燃させて CO、HC を CO₂、H₂O にするサマルリアクターや触媒コンバーターなどの各種の浄化装置が実用化されている。

従来、排ガス浄化装置等において、高温の腐食性ガス雰囲気を用いられる熱交換器は、耐食性を有するステンレス鋼材からなる接合部材が Cu 系ろう材によってろう接されて製作される。前記 Cu 系ろう材は、1000℃ 以上の融点を持つ、耐食性の良好な銅ろうや、特開昭 60-72895 号公報に記載された Mn : 5 ~ 20 %、あるいはさらに N i : 1 ~ 5 %、残部実質的に Cu からなるろう材が用いられてきた。

【0003】最近、排ガス組成の変化などによって熱交換器内の腐食環境が一段と厳しくなっており、排ガスの凝縮による腐食の問題も生じている。このため、熱交換器の流路構造を構成する接合部材同士がろう材によって接合されるろう接部に対して耐食性のより一層の向上が求められている。このような要求に対して、国際公開 WO00/45987 号に記載されているように、本発明者はステンレス鋼材からなる基板に、純 N i あるいは N i を主成分とする N i 基合金で形成された F e 原子拡散抑制層、および純 Cu あるいは Cu を主成分とする Cu 基合金によって形成されたろう材層を積層したろう接用複合材およびこれを素材とする接合部材を用いて、熱交換器の流路構造を構成することが提案されている。このろう接用複合材によれば、F e 原子拡散抑制層により、ろう接の際にステンレス鋼材から F e 原子がろう材部に拡散することが抑制され、また F e 原子拡散抑制層から過量の N i がろう材部に拡散して Cu - N i 合金を形成して、ろう材部の耐食性を向上させることができる。

【0004】

【発明が解決しようとする課題】上記のように、F e 原子拡散抑制層を備えらるろう接用複合材を用いることにより、熱交換器のろう材部における耐食性を向上させることができた。しかしながら、その後の更なる研究により、高温排気ガスの熱交換を行う熱交換器においては、単にろう材部の耐食性を向上させるだけでは耐久性とし

て不十分であり、また熱交換器を組み込んだ処理システム全体にとって悪影響があることがわかった。すなわち、排ガスなどの熱交換すべき流体が高温腐食性流体である場合、ろう材部の耐酸化性が不足すると、ろう材部の酸化減耗により接合強度の劣化が生じるばかりでなく、酸化皮膜がろう材部の表面から剥離して熱交換器の下流側へ流れて行き、下流側に設けられた各種の処理装置を汚損し、その性能を劣化させるという問題が判明した。

【0005】本発明はかかる問題に鑑みなされたもので、熱交換器の流路構造等のろう接構造において、そのろう材部に優れた耐食性および耐酸化性を付与することができるろう接用材料、およびろう材部における耐食性および耐酸化性に優れたろう接構造を提供することを目的とするものである。

【0006】

【課題を解決するための手段】本発明によるろう接用複合材は、耐食性鋼材により形成された基板と、前記基板の表面に積層形成され、純CuあるいはCuを主成分とするCu基合金で形成されたCu系ろう材によって接合部材をろう接する際に前記基板からFe原子がろう材側に拡散するのを抑制するFe原子拡散抑制層とを備え、前記Fe原子拡散抑制層はNiを主成分とし、Cr:10~30mass%を含有するNi-Cr合金で形成されたものである。以下、成分の単位は単に%で表示する。

【0007】この複合材によれば、基板にはFe原子拡散抑制層が積層形成されているので、この複合材を用いてろう接したろう接構造物におけるろう材部には、ろう接の際に基板からFe原子がろう材部に拡散することがFe原子拡散抑制層によって防止され、ろう材部の耐食性の劣化を防止することができる。さらに、Fe原子拡散抑制層はCrを所定量含むNi-Cr合金で形成されているので、ろう接の際にFe原子拡散抑制層からNi、Crをろう材部に拡散させることによって、ろう材部に15~25%のNi、10~15%のCrを含有したCu-Ni-Cr合金を形成することができる。前記Cu-Ni-Cr合金のNiはろう材部の耐食性をより一層向上させ、前記Crはろう材部の表面にCr系酸化膜を形成して、耐酸化性を向上させる。このため、ろう接構造のろう材部を耐食性および耐酸化性に優れたものとすることができる。

【0008】前記ろう接用複合材の好ましい態様として、前記Fe原子拡散抑制層の上に前記Cu系ろう材によって形成されたろう材層を積層形成することができる。ろう材層を一体的に設けることにより、接合部材をろう接する際に、別途、ろう材を準備する必要がなく、ろう接作業性を向上させることができる。

【0009】また、前記ろう接用複合材の好ましい態様として、Cu系ろう材をCuを主成分とし、Al:1~7%を含有するCu基合金で形成することができる。か

かるAl含有Cu基合金を用いることにより、Al系酸化膜がCr系酸化膜の下側に形成され、2重の酸化膜により耐酸化性を著しく向上させることができる。

【0010】前記ろう接用複合材におけるFe原子拡散抑制層は、5μm以上の厚さとすることが好ましい。5μm以上の厚さとするこ

とで、ろう接の際に基板のFe原子がFe原子拡散抑制層を固相拡散してろう材部に侵入するのを十分に抑制することができ、ろう材部のFe原子の拡散侵入による耐食性の劣化を十分に防止することができる。

【0011】本発明によるろう接構造は、耐食性鋼材で形成された基板を有する第1接合部材と、耐食性鋼材で形成された基板を有し、前記第1接合部材にろう材部を介してろう接された第2接合部材とを備え、前記第1接合部材は前記第2接合部材からろう接される際に前記第1接合部材の基板からFe原子がろう材部に拡散するのを抑制するFe原子拡散抑制層を有し、このFe原子拡散抑制層はNiを主成分とし、Cr:10~30mass%を含有するNi-Cr合金で形成され、前記ろう材部はCuを主成分とし、Ni:15~25%、Cr:10~15%を含有するCu-Ni-Cr合金で形成される。

【0012】このろう接構造によれば、第1接合部材は基板に必須成分としてCrを含むNi-Cr合金で形成されたFe原子拡散抑制層が形成されているので、第2接合部材をろう接する際に、第1接合部材の基板からFe原子がろう材部に拡散侵入することを抑制することができ、さらにFe原子拡散抑制層からのNi、Crの拡散によって形成された所定量のNiによる合金化と、所定量のCrによるCr系酸化膜の形成により、ろう材部に優れた耐食性と耐酸化性とが付与される。これによって、ろう接構造は優れた耐久性を備えたものとなる。

【0013】前記ろう接構造において、そのろう材部はCuを主成分とし、Ni:15~25%、Cr:8~15%、Al:1~5%を含有するCu-Ni-Cr-Al合金で形成することが好ましい。ろう材部に所定量のAlを含有させておくことで、Al酸化膜をCr系酸化膜の下側に複合形成することができ、耐酸化性をより向上させることができる。ろう材部に所定量のAlを含めるには、ろう接に用いるCu系ろう材として、Alを1~5%含有し、Cuを主成分とするAl添加Cu基合金を用いられる。

【0014】前記ろう接構造において、前記第1接合部材と前記第2接合部材との間にこれらの接合部材によって区画された流路を形成することができる。かかる流路を形成することにより、この流路に熱交換される流体あるいは熱交換する媒体を流すことができ、優れた耐久性を備えた熱交換器の流路構造を提供することができる。また、前記流路の下流側に付設される装置に対して酸化皮膜の剥離による悪影響を防止することができる。

【0015】また、前記ろう接構造において、前記第2

部材も前記第1接合部材と同様、前記第1接合部材と第2接合部材とがろう接される際に前記第2接合部材の基板からF e原子がろう材部に拡散するのを抑制するF e原子拡散抑制層を設け、このF e原子拡散抑制層を前記N i-C r合金によって形成することができる。これによって、第2接合部材からろう材部にF e原子が拡散侵入するのを防止することかでき、また第2接合部材のろう接性を向上することができる。

【0016】

【発明の実施の形態】図1は本発明の実施形態にかかるろう接用複合材1を示しており、プレート状の基板11の片面にF e原子拡散抑制層12が積層形成され、その上にろう材層13が積層形成されている。このろう接用複合材1は、F e原子拡散抑制層12の上のろう材層13が積層形成されているので、ろう接作業を行う際に、別途準備したろう材をろう接の対象である接合部材の間に付設するといった煩雑な作業が不要となり、ろう接作業性に優れる。

【0017】前記基板11は、耐食性の良好な鉄鋼材、例えばJ I S規格のSUS304、SUS316等のオーステナイト系ステンレス鋼材、SUS430、SUS434等のフェライト系ステンレス鋼材などのステンレス鋼材で形成される。

【0018】前記F e原子拡散抑制層12は、C r:10~30%、好ましくはC r:15~25%、残部N iを本質的成分とするN i-C r合金で形成される。このN i-C r合金は、F eを含み、その融点かろう材層13を形成するC u系ろう材の融点よりも高く、N iおよびC rが前記ろう材の主成分であるC uと固溶し、従って腐食の起点になりやすい析出物を生成しないものである。前記N i-C r合金は、典型的には本発明において重要成分であるC rのほか、残部N iおよび不可避的不純物元素からなるが、N iに固溶し、N i-C r合金としての加工性を損なわず、ろう接後のろう材の特性を劣化させない元素であれば、その微量添加は許容される。

【0019】前記N i-C r合金のN iはろう接の際にろう材層13の溶融により生じたろう材部に15~25%程度拡散させて固溶させることにより、ろう材部の耐食性を向上させる。一方、C rは前記ろう材部に10~15%拡散させて固溶させることにより、その表面にC r系酸化膜を形成するようになるため、耐酸化性を向上させる。前記N i-C r合金のC r含有量が10%未満ではろう接の際にろう材部に前記過量のC rの拡散が困難であり、ろう材部の耐酸化性が低下するようになる。一方、30%を超えるとう加工性が劣化し、ろう材部への拡散が過多となる。その結果、ろう材部におけるC r量が15%超になり、C rの偏析が生じ易くなり、耐食性が却って低下するようになる。このため、F e原子拡散抑制層12を形成するN i-C r合金のC r含有量を1

0~30%、好ましくは10~25%、より好ましくは15~25%とする。

【0020】前記F e原子拡散抑制層12の厚さは、5 μ m以上、好ましくは8 μ m以上、より好ましくは10 μ m以上とするのがよい。前記ろう接用複合材を用いて、ろう接する場合、ろう接温度は後述するように1100~1250℃程度とされるが、かかる高温でのろう接によっても、5 μ m程度の厚さがあれば相当量のF e原子の拡散抑制効果を得ることかでき、10 μ mあればほぼ完全にF e原子のろう材部への拡散を防止することができる。

【0021】前記ろう材層13としては、純C uあるいはC uを主成分とするC u基合金からなるC u系ろう材によって形成される。前記C u基合金としては、構成成分が完全に固溶状態をなす、例えばC u-N i合金、C u-Mn-N i合金を用いることができる。C u含有量は、概ね85%程度以上あればよい。前記C u-N i合金では、N i:15%以下、残部C uを本質的成分とする組成が好ましい。N iが15%超になるとろう材の融点が高くなり、ろう接作業が困難になる。前記C u基合金には、C uに固溶し、ろう材の加工性、ろう接後のろう材部の特性を損なわない元素であれば、その微量添加は許容される。

【0022】前記C u系ろう材は、特にA1が1~5%、好ましくは2~4%添加されたA1添加C u基合金が好ましい。A1を添加することによって、ろう接によって形成されたろう材部の表面に形成されたC r系酸化膜の下側(ろう材側)にさらにA1系酸化膜が形成されるようになり、2重の酸化膜が形成されるため耐酸化性が著しく向上する。A1量が1%未満ではA1系酸化膜の形成が困難であり、一方5%を超えるとA1添加C u基合金の加工が困難となり、ろう材として使用できないようになる。A1添加C u基合金をろう材として用いる場合、A1の作用により耐酸化性が大幅に向上するので、ろう材部におけるC r含有量を8~15%とすることで十分な耐酸化性を得ることができる。なお、前記C r系酸化膜やA1系酸化膜は、E P M Aによって確認することができる。

【0023】前記基板11へのF e原子拡散抑制層12の積層形成には、一般的には圧接によるクラッド法が適用されるが、めっき、溶射、P V D、C V Dなどの種々の方法を適用することもできる。基板11とF e原子拡散抑制層12とを圧接によってクラッドすれば、めっきの場合に問題となるピンホールが生じることもなく、両者を容易に一体化することかでき、工業的生産性に優れる。また、圧接の際の圧下率を調整するだけでF e原子拡散抑制層12の厚さも容易に制御することができる。ろう材層13は、通常、基板11に積層されたF e原子拡散抑制層12の上に圧接により接合される。3層を圧接によりクラッドする場合、基板11、F e原子拡散抑

制層12およびろう材層13の各素材をおのおの重ね合わせて圧接し、必要に応じて拡散焼鈍すればよい。

【0024】前記ろう接複合材を用いる場合のろう接温度は、Cu系ろう材の融点以上でFe原子拡散抑制層を形成する金属の融点未満の温度とすればよいが、通常、1100～1250℃程度、好ましくは1150～1200℃程度とされる。1100℃未満ではFe原子拡散抑制層からNi、Crがろう接の際にろう材部に拡散するのに時間がかかり生産性に劣る。一方、1250℃超の温度では不必要に高温過ぎて、加熱炉の損傷が激しく、あるいは非常に耐熱性に富んだ高価な炉が必要になり、いずれにしても工業的生産に適さない。ろう接温度における保持時間は、1100～1250℃程度であれば、10～50分程度でよい。このろう接時の温度保持の際に、ろう接用複合材が適宜の形状に加工される場合、その基板11の焼鈍も同時に行われる。

【0025】以上、本発明のろう接用複合材を実施形態により説明したが、本発明はこれによって限定的に解釈されるものではない。例えば、上記実施形態では、基板11の片側にFe原子拡散抑制層12およびろう材層13を積層形成したが、基板の両面に接合部材がろう接されるような用途に使用する場合には、図2に示すろう接用複合材1Aのように、基板11の両面にFe原子拡散抑制層12、12およびろう材層13、13を積層することができる。また、ろう材を別途準備する場合には、ろう材層13を積層する必要はない。

【0026】ここで、上記ろう接用複合材1を用いてろう接したろう接構造物のろう材部の耐食性、耐酸化性の調査結果について説明する。調査に用いたろう接用複合材1は、JIS規格のSUS304ステンレス鋼板(板厚0.4mm)を基板11とし、その上にNi-Cr合金からなるFe原子拡散抑制層12および純CuあるいはCu-A1合金からなるろう材層13を圧接により積層形成したものである。各試料について用いた複合材のFe原子拡散抑制層12のNi-Cr合金中のCr量、ろう材層13のCu-A1合金中のAl量、ろう接条件(温度、保持時間)、ろう材部のCu-Ni-Cr合金あるいはCu-Ni-Cr-A1合金中のNi量、Cr量およびAl量を表1(元素量の単位はmass%)に示

す。なお、ろう材層をCu-7%A1合金で形成することを試みたが、この合金は加工性が悪く、板状に加工することができなかったため、ろう接用複合材を製作するには至らなかった。

【0027】この複合材をろう材層13側が外側になるようにL字形に折り曲げてL形部材を製作した。このL形部材の一对を図3に示すようにL形部材5の端辺を重ね合わせてろう接し、T字形のろう接構造物試料を得た。このようにして製作された各試料を用いて、ろう材部の平均組成をEPMAによって測定するとともに、耐食性試験および耐酸化性試験を行った。

【0028】耐食性試験は、非酸素凝縮液を模擬した下記組成の模擬凝縮水を調製し、100℃の模擬凝縮水中に各試料を500h浸漬後のろう材部が露出した試料のT形上面を肉眼観察し、腐食が皆無のものを優(A)、表面の腐食領域が20%以下のものを良(B)、表面の腐食領域が20%超のものを不可(C)と評価した。

・模擬凝縮水組成(pH4.4)

Cl⁻: 20ppm、SO₄²⁻: 350ppm、NO₃⁻: 150ppm、NH₄⁺: 700ppm、辛酸: 500ppm、酢酸: 700ppm

【0029】一方、耐酸化性試験は、各試料を大気中で850℃で50h保持した後の質量変化を測定し、ろう材部が露出した試料のT形上面の面積で除して1cm²当たりの酸化増減量を求めた。試験後の試料のろう材部において、表面酸化皮膜が粉状に脱落した場合、粉状酸化皮膜を刷毛によって除去して測定した。この場合、酸化増減量は負値で示される。ろう材部の表面に安定酸化膜が形成されている場合には、酸化増減量は正値で示される。耐酸化性の評価は、酸化増減量が正値で、基板のSUS304(1mq/cm²程度)と同等あるいはそれ以下の場合を優秀(AA)、SUS304よりも増加量がやや多い場合を優(A)、酸化皮膜が脱落には至っていないが質量増加が大きい場合を良(B)、酸化皮膜が一部脱落した場合を不可(C)、酸化皮膜の脱落が著しい場合を不可(CC)と評価した。これらの結果を表1に併せて示す。

【0030】

【表1】

試料 No.	Fe原子 拡散抑制層 Cr%	ろう材層 Al%	ろう接条件 温度 時間 ℃ h	ろう材組成 Ni% Cr% Al%	耐食性 評価	耐酸化性 増減量 mg/cm ²	評価
* 1	—	—	1180 20	20 —	A	-18.5	C C
* 2	2	—	1180 20	19 1	A	-18.4	C C
* 3	5	—	1180 20	18 2	A	-10.2	C C
* 4	10	—	1180 20	18 8	A	-8.5	C
5	15	—	1180 20	18 10	A	3.2	B
6	20	—	1180 20	17 12	A	2.8	A
7	25	—	1180 20	14 14	B	2.0	A
* 8	10	—	1100 20	8 5	C	-9.48	C C
* 9	10	—	1200 20	18 8	A	-8.70	C
10	10	—	1250 20	22 10	A	3.1	B
11	20	—	1100 40	15 11	A	3.0	B
* 12	20	—	1260 40	28 18	C	1.13	A
21	10	1	1180 20	18 8	A	4.3	B
22	10	2	1180 20	18 8	A	2.7	A
23	10	3	1180 20	17 8	A	0.56	A A
24	10	5	1180 20	16 8	A	0.41	A A
25	20	1	1180 20	17 12	A	1.12	A
26	20	2	1180 20	17 12	A	0.42	A A
27	20	3	1180 20	17 12	A	0.30	A A
28	20	5	1180 20	16 12	A	0.28	A A

(注) 試料No. に「*」を付したものは比較例、他は発明例

【0031】表1の試料No. 1〜7より、ろう接温度を加熱限界温度より十分に余裕のある1180℃でろう接した場合、Fe原子拡散抑制層をCr:15〜25%含有したNi-Cr合金で形成した発明例(試料No. 5〜7)では、20分間程度の比較的短時間の保持により、ろう材部におけるCr量が10〜14%となり、良好な耐食性と耐酸化性を備えることがわかる。一方、試料No. 8〜10より、Fe原子拡散抑制層を比較的低Cr量の10%とした場合、比較的短時間の加熱では、ろう接温度を加熱限界温度付近の1250℃に上げることにより、ろう材部のCr量として10%確保することができ、耐酸化性も実用レベルのものが得られることがわかる。もっとも、No. 11より、ろう接温度を1100℃としても、Fe原子拡散抑制層をCr量の高いNi-Cr合金で形成し、ろう接時間を比較的長くすることで、良好な耐酸化性が得られることがわかる。また、試料No. 21〜28より、ろう材としてAl量が1〜5%、特に2〜5%のAl-Cu合金ろう材を用いることにより、耐酸化性が顕著的に向上することが確認された。

【0032】次に、上記実施形態にかかるろう接用複合材1、1Aを素材として用いたろう接構造の実施形態として熱交換器の流路構造を説明する。

【0033】図4は第1実施形態にかかる熱交換器の流路構造を示す斜視図である。対向して配置された一組の

プレート部材21-1、21-2が所定の間隔を隔てて複数組平行に配置され、互いに隣接する二組のプレート部材において、図例では上側組の下側のプレート部材21-2と、このプレート部材21-2に対向して配置された下側組の上側のプレート部材21-1との間に、断面が波形に屈曲形成された蛇腹状のフィン部材22が介設されている。なお、前記プレート部材は本発明のろう接用構造の第1接合部材に、フィン部材は第2接合部材に対応する。

【0034】前記一組のプレート部材21-1、21-2の間の空間部が冷却水等の熱交換媒体が流れる媒体流路とされる。一方、上側組の下側のプレート部材21-2と下側組の上側のプレート部材21-1との間で、前記フィン部材22により仕切られた多数の部分空間部が排ガス等の熱交換される高温腐食性ガスが流れるガス流路とされる。

【0035】各フィン部材22は、波形凸部の最上部とこのフィン部材22を挟持する上側のプレート部材21-2の下面とからろう材部を介してろう接され、また波形凹部の最下部とフィン部材22を挟持する下側のプレート部材21-1の上面とが同様にろう材部を介してろう接されている。以下の説明において、一組のプレート部材21-1、21-2について、両者を区別しない場合、プレート部材の符号として21を用いて説明する場合、

合がある。

【0036】前記プレート部材21のろう接合部材は、図1に示す構造、材質を有するろう接合部材1が適宜の大きさに加工されたものである。前記フィン部材22は、ろう接合部材1の基板11と同様のステンレス鋼からなる薄板を波形に加工されたものである。説明の便宜上、プレート部材用素材について前記プレート部材21と同様の符号を用い、またその各種層部についてはろう接合部材1と同様の符号を付することとする。

【0037】プレート部材用素材21およびフィン部材22を用いて、熱交換器を製作するには、フィン部材22がプレート部材用素材21のろう材層13に当接するように、フィン部材22とプレート部材用素材21とを交互に重ね合わせて図4のようになり組み立てて保形し、この組立体を真空中あるいは還元ガス雰囲気中でF e原子拡散抑制層12の融点未満でろう材層13の融点以上の温度、通常、1100〜1250℃で、ろう材部の本質的成分がNi:15〜25%、Cr:10〜15%(後述するA1添加Cu基合金をろう材によりろう接する場合)は8〜15%、残部Cuとなるように10〜50分間程度加熱保持する。これによって、プレート部材用素材21のろう材層13が溶融し、基板11に圧接されたF e原子拡散抑制層12に前記Ni、Cr量を含む良好な耐食性、耐酸化性を備えたいろう材部を介してフィン部材22がろう接される。Cu系ろう材として1〜5% A1のA1含有Cu基合金を使用することで、ろう材部にはほぼ同量のA1が含有し、耐食性を劣化させることなく、耐酸化性を著しく向上させることができる。この場合、Cr量は少なくとも8%有れば良好な耐酸化性を得ることができる。

【0038】図5は第2実施形態にかかる熱交換器の流路構造を示す断面図である。この流路構造はハニカム構造をしており、台形状の凹部32と凸部33とが交互に連続して波形に成形加工された凹凸部材31が上下方向に複数積層されて構成されている。説明の便宜上、上下に隣接配置された一対の凹凸部材に対して31-1、31-2の符号を付する。なお、前記凹凸部材31-1、31-2は本発明のろう接構造の第1接合部材、第2接合部材に対応する。

【0039】上下に隣接する凹凸部材31-1、31-2同士は上側の波部材31-1-1の凹部32の外周(下面)と、下側の凹凸部材31-2の凸部33の外周(上面)とが互いにろう接されている。これによって上側の凹凸部材31-1の凸部33と下側の凹凸部材31-2の凹部32との間には6角形断面の空間部が多数形成される。この空間部が排ガス等の高温腐食性ガスが流れるガス流路Gと、冷却水等の熱交換媒体が流れる媒体流路Wとされ、図例ではガス流路Gと媒体流路Wとは左右に交互に配置されている。

【0040】前記熱交換器の凹凸部材31の素材は、図

2に示す断面構造、材質を有するろう接合部材1Aが適宜の大きさに凹凸状に成形加工されたものである。説明の便宜上、凹凸部材用素材について前記凹凸部材31と同様の符号を用い、またその各種層部についてはろう接合部材1Aと同様の符号を付することとする。

【0041】前記凹凸部材用素材31を用いて、熱交換器を製作するには、上側の凹凸部材用素材31-1の下板部32と、下側の凹凸部材用素材31-2の上板部33とを重ね合わせて図5に示すように積層し、第1実施形態と同様に真空中あるいは還元ガス雰囲気中で加熱保持すればよい。これによって、上下に対向配置された凹凸部材用素材31-1、31-2のろう材層13、13同士が溶融し一体化し、所定量Ni、CrさらにはA1を含むろう材部を介して互いにろう接される。

【0042】本発明のろう接構造はかかる第1、第2実施形態の熱交換器の流路構造により限定的に解釈されるものではない。例えば、第1実施形態のプレート部材21の積層段数、第2実施形態の凹凸部材31の積層段数は、要求に応じて自由に設定することができる。また、上記第1実施形態では、フィン部材22はステンレス鋼薄板を用いたが、フィン部材についてもステンレス鋼薄板を基板としてF e原子拡散抑制層を積層形成したもの、さらには図1と同様に、F e原子拡散抑制層の上のろう材部を形成したものを用いてもよい。フィン部材についてもF e原子拡散抑制層を形成することで、ろう接の際に、フィン部材の基板からF e原子が溶融したろう材に拡散侵入するのを防止することができ、フィン部材がろう接されたろう接部の耐食性劣化を防止することができる。

【0043】また、上記第1、第2実施形態の熱交換器の流路構造では、素材として用いたろう接合部材1、1AにはF e原子拡散抑制層12のほか、ろう材層13がクラッドされているが、ろう材層13は必ずしも必要ではない。この場合、別途準備したCu系ろう材をプレート部材用素材とフィン部材との間、あるいは凹凸部材用素材の間に付設して、ろう接すればよい。

【0044】【発明の効果】本発明のろう接合部材は、耐食性鋼材で形成された基板にNiを主成分とし、Crを10〜30%含有したNi-Cr合金で形成されたF e原子拡散抑制層を備えることで、Cu系ろう材を用いて接合部材をろう接する際、ろう材部に耐食性を劣化させるF e原子の拡散を抑制することができるとともに、適量のNiおよびCrを容易に拡散させることができ、ろう材部の耐食性、耐酸化性を向上させることができる。このため、本発明のろう接合部材を用いて、排ガス等の高温腐食雰囲気下において使用される熱交換器の流路構造を構成することにより、その耐久性を向上させることができる。

【図面の簡単な説明】

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【図 1】本発明の実施形態にかかるろう接用複合材の部分断面図である。

【図 2】他の実施形態にかかるろう接用複合材の部分断面図である。

【図 3】耐食性および耐酸化性試験に用いた T 字形のろう接構造物の断面図である。

【図 4】本発明のろう接構造の第 1 実施形態にかかる熱交換器の流路構造を示す部分断面図である。

【図 5】本発明のろう接構造の第 2 実施形態にかかる熱*

* 交換器用の流路構造を示す部分断面図である。

【符号の説明】

1、1A ろう接用複合材

11 基板

12 Fe 原子拡散抑制層

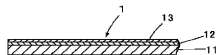
13 ろう材層

21-1、21-2 プレート部材

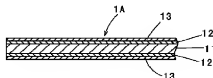
22 フィン部材

31 凹凸部材

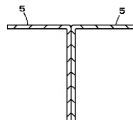
【図 1】



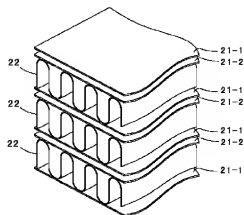
【図 2】



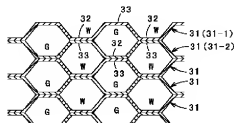
【図 3】



【図 4】



【図 5】



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